IV. SUMMARY

This paper has presented experimental evidence that:

(a) The distance from which the ions are collected in front of the sampling probe is approximately 1 mm, regardless of the container geometry and dimensions.

(b) The average time available for reaction of the ions collected and observed does not vary significantly with pressure and is on the order of 0.3 μsec.

(c) A large fraction of the sheath potential is dropped in a distance from the wall that is less than a reaction mean free path.

A technique was presented to measure collection distance of positive ions from a plasma. This technique is useful in determining the collection distance if:

(1) The ions arriving at walls of probe (orifice) are representative of those arriving at the container walls.

(2) The collection distance (or equivalently, reaction time) of the observed ions varies with pressure in the particular discharge and associated apparatus employed.

Since the time available for reaction does not vary significantly with pressure with the reported apparatus, ion–molecule reactions occurring in the plasma in these and similar systems can be investigated by pressure variation, especially if the reaction time is calibrated first by a reaction whose cross section is accurately known.

ACKNOWLEDGMENTS

Photoionization of 1,3-Butadiene, 1,2-Butadiene, Allene, and Propyne*

ALBERT C. PARR AND FRED A. ELDER

Department of Physics, The University of Chicago, Chicago, Illinois

(Received 8 May 1968)

Using a photoionization mass spectrometer, the ionization potentials of the parent molecules and the appearance potentials of the fragment ions, observed below 13 eV, have been determined for 1,3-butadiene, 1,2-butadine, allene, and propyne. The ionization potentials of 1,3-butadiene are 9.07±0.02 eV, 9.80±0.04 eV, and 11.7±0.04 eV. The adiabatic ionization potential of 1,2-butadiene is 9.23±0.02 eV. The adiabatic ionization potential of allene is 9.62±0.04 eV. The ionization potentials of propyne are 10.38±0.02 eV and 11.30±0.02 eV. The heat of formation of $C_3H_3^+$ and $C_4H_5^+$ is calculated to be 11.18±0.04 eV and 10.45±0.04 eV, respectively. Derived bond energies for the ionic states are given. The data are shown to be consistent with rearrangement of 1,3-butadiene via hydrogen migration in the excited molecular ion. At threshold for fragmentation, the $C_4H_5^+$ and $C_3H_3^+$ ions from 1,3-butadiene and 1,2-butadiene are identical.

INTRODUCTION

Collin and Lossing[1] have suggested that the $C_3H_3^+$ ion from 1,3-butadiene, 1,2-butadiene, allene, propyne, 1-butyne, and 2-butyne is the same in each case. They concluded that the $C_3H_3^+$ ion had the propargyl structure $(CH \equiv C{-}^+CH_2)$ in each case and that hydrogen migration which is necessary to form $C_3H_3^+$ in 1,3-butadiene occurs with almost zero activation energy. The butadienes were studied further by King[2] who suggested that above the ionization onset, the excess energy provides activation energy such that the H atoms on the carbon skeleton are mobile. According to

this picture an H atom may migrate on the 1,3-butadiene, forming a molecule–ion such that the $C_3H_3^+$ fragment is the same as that from 1,2-butadiene where presumably $C_3H_3^+$ is formed by a simple bond cleavage.

Bergmann and Demtröder[3] have studied 1,3-butadiene utilizing a mass spectrometer to study the photodissociation of the neutral molecule. To explain the fragments they observe, they suggest that 1,3-butadiene rearranges to an excited state of 1,2-butadiene or butyne from which it fragments.

The photoionization efficiency curves for 1,3-butadiene, 1,2-butadiene, allene, and propyne and their fragments have been measured in an attempt to further check the proposed rearrangement in 1,3-butadiene and to obtain more precise heats of formation and dissociation energies.

[1] J. Collin and F. D. Lossing, J. Am. Chem. Soc. **79**, 5848 (1957); **80**, 1568 (1958).
[2] A. B. King, J. Phys. Chem. **68**, 6 (1964).
[3] K. Bergmann and W. Demtröder, J. Chem. Phys. **48**, 18 (1968).

TABLE I. Ionization and appearance potentials.

Substance	Ion	This work	Interpretation	Other photoionization	Electron impact	Spectroscopic
1,3-Butadiene	$C_4H_6^+$ $m/e = 54$	9.07 ± 0.02	Adiabatic ionization potential	9.07 ± 0.01^a 9.075 ± 0.005^b	9.33 ± 0.1^c 9.18 ± 0.02^d	9.07^e
	$C_4H_6^+$ $m/e = 54$	9.80 ± 0.04	Higher ionization potential			
	$C_4H_6^+$ $m/3 = 54$	11.70 ± 0.05	Higher ionization potential			
	$C_4H_5^+$ $m/e = 53$	11.56 ± 0.04	Appearance potential	11.39 ± 0.05^b	12.03^c	
	$C_3H_3^+$ $m/e = 39$	11.40 ± 0.02	Appearance potential	11.35 ± 0.05^b	11.65^c 11.71^d	
1,2-Butadiene	$C_4H_6^+$ $m/e = 54$	9.23 ± 0.02	Adiabatic ionization potential		9.57 ± 0.02^d	
	$C_4H_5^+$ $m/e = 53$	11.04 ± 0.04	Appearance potential			
	$C_3H_3^+$ $m/e = 39$	10.86 ± 0.04	Appearance potential		11.00 ± 0.03^d	
Allene	$C_3H_4^+$ $m/e = 40$	9.62 ± 0.04	Adiabatic ionization potential			
	$C_3H_4^+$ $m/e = 40$				10.16 ± 0.02^d	10.19 ± 0.01^f
	$C_3H_3^+$ $m/e = 39$	11.48 ± 0.02	Appearance potential		12.02 ± 0.03^d	
Propyne	$C_3H_4^+$ $m/e = 40$	10.38 ± 0.02	Adiabatic ionization potential	10.36^g	10.48 ± 0.06^h	10.36^i
	$C_3H_4^+$ $m/e = 40$	11.30 ± 0.02	Higher ionization potential			11.31^j
	$C_3H_3^+$ $m/e = 39$	11.55 ± 0.02	Appearance potential		12.00 ± 0.05^d	

[a] K. Watanabe, J. Chem. Phys. **22**, 1564 (1954).
[b] B. Brehm, Z. Naturforsch. **21a**, 196 (1966).
[c] A. B. King, J. Phys. Chem. **68**, 1409 (1964).
[d] J. Collin and F. P. Lossing, J. Am. Chem. Soc. **79**, 5848 (1957).
[e] W. C. Price and A. D. Walsh, Proc. Roy. Soc. (London) **174**, 720 (1940).
[f] L. H. Sutcliffe and A. D. Walsh, J. Chem. Soc. **1952**, 894.
[g] K. Watanabe, J. Chem. Phys. **26**, 542 (1957).
[h] J. L. Franklin and F. H. Field, J. Am. Chem. Soc. **76**, 1994 (1954).
[i] T. Nakayama and K. Watanabe, J. Chem. Phys. **40**, 558 (1964).
[j] W. C. Price and A. D. Walsh, Trans. Faraday Soc. **41**, 381 (1945).

EXPERIMENTAL PROCEDURE

The photoionization mass spectrometer was the same as reported earlier[4] with the exception of a new light source. The hydrogen many-line spectrum is produced in a dc discharge with typical operation at 1.6 A and 780 V across the discharge tube. The bandpass of the monochromator was 3 Å for all experiments reported here.

The 1,3-butadiene, propyne, and allene were obtained from the Matheson Company.[5] The 1,2-butadiene was obtained from the American Petroleum Institute as a standard sample.

RESULTS

Table I gives the ionization onsets and appearance potentials of the ionic species studied. The electron-impact data are included for completeness and, as is usually the case, the ionization potentials and appearance potentials determined by electron impact are higher than the more accurate photoionization data. Also, as usual, the ionization potentials agree with the spectroscopic values, though in some cases it was
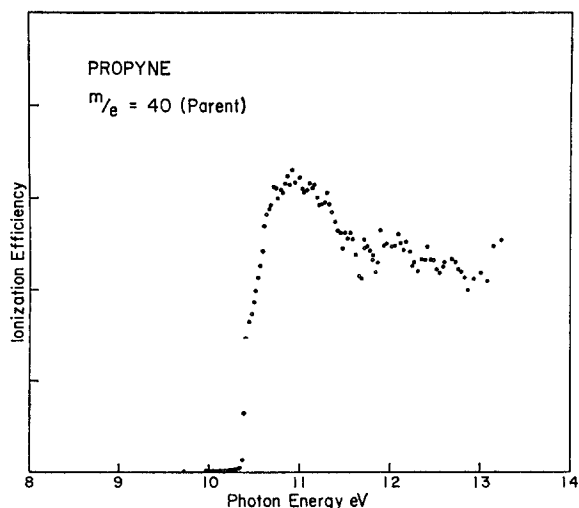

FIG. 1. Photoionization efficiency curve of propyne. Vertical scale is in arbitrary units and horizontal scale in electron volts.

PROPYNE
$m/e = 40$ (Parent)

Ionization Efficiency

Photon Energy eV

TABLE II. Relative intensities.

Ion	1,3-Butadiene	1,2-Butadiene	Allene	Propyne
54	1	1	...	...
53	0.13	0.085	...	...
40	...	...	1	1
39	0.84	0.21	0.18	0.09
Energy	12.52 eV	11.98 eV	12.50 eV	12.57 eV

[4] B. Steiner, C. F. Giese, and M. G. Inghram, J. Chem. Phys. **34**, 186 (1961).

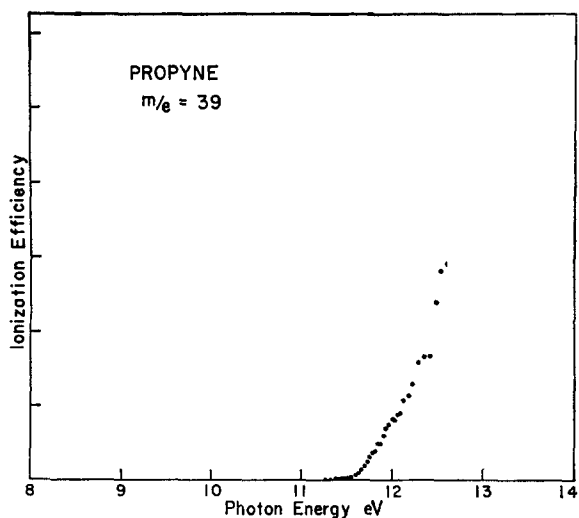[5] Matheson Company, East Rutherford, N.J.

FIG. 2. Photoionization efficiency curve of $C_3H_3^+$ from propyne. Vertical scale is in arbitrary units and horizontal scale in electron volts.
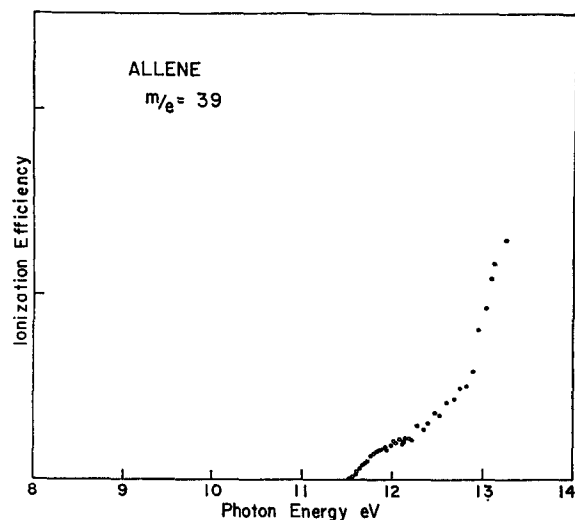

FIG. 4. Photoionization efficiency curve of $C_3H_3^+$ from allene. Vertical scale is in arbitrary units and horizontal scale in electron volts.

discovered that the spectroscopic value referred to an excited state of the ion. Figures 1–10 give the ionization efficiency curves for the parent and fragment ions studied in the energy region from onset to 13 eV. The statistics of the data points are approximately 2%. Table II gives the relative intensities of the various ions observed.

The difference in photon energies at which the relative intensities are given (0.54 eV for 1,3-butadiene and 0.07 eV for allene and propyne) is the difference between the heat of formation of the neutral compounds. Thus the photon energies correspond to the same total energy for the respective pairs of molecules.

The propyne parent curve is shown in Fig. 1. The ionization threshold is at 10.38 eV. The threshold is

followed by a series of breaks and peaks in the ionization efficiency curve. Figure 2 shows that fragmentation starts at 11.55 eV. Thus the structure between threshold and 11.55 eV is real and can be ascribed to autoionization.

Price and Walsh,[6] from two Rydberg series, reported the ionization potential of propyne as 11.31 eV. Nakayama and Watanabe[7] reported a Rydberg series converging to 10.36 eV and a photoionization threshold of 10.36 eV in agreement with the present work. These authors did not observe the Rydberg series reported by
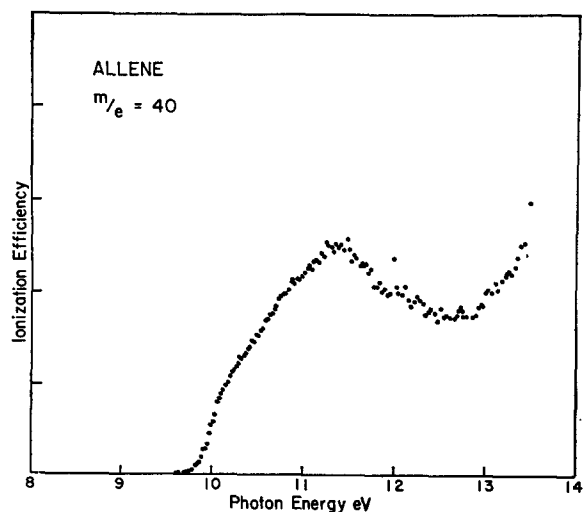

FIG. 3. Photoionization efficiency curve of allene. Vertical scale is in arbitrary units and horizontal scale in electron volts.
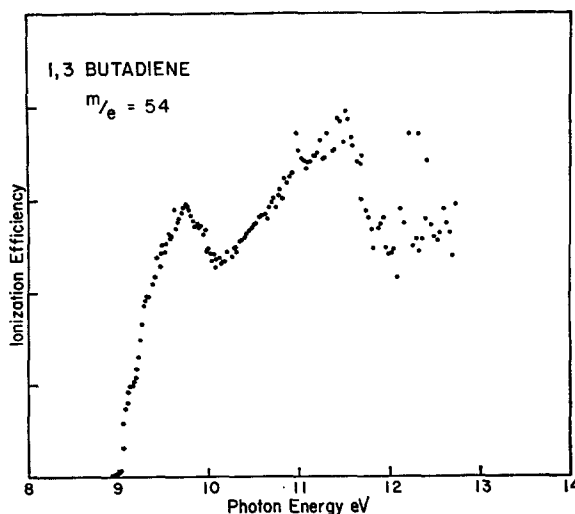

FIG. 5. Photoionization efficiency curve of 1,3-butadiene. Vertical scale is in arbitrary units and horizontal scale in electron volts.

[6] W. C. Price and A. D. Walsh, Trans. Faraday Soc. 41, 381 (1945).
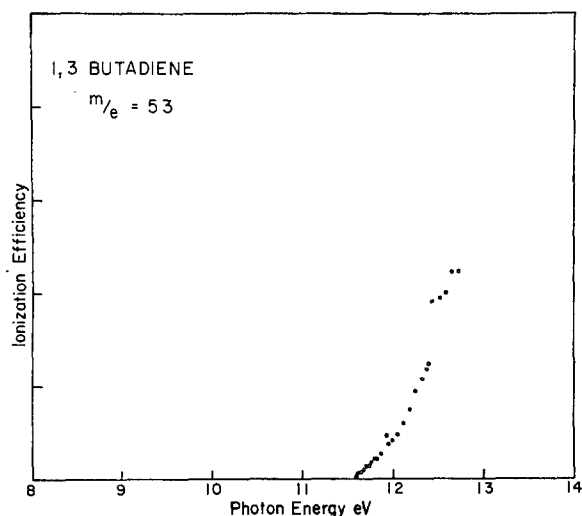[7] K. Watanabe and T. Namioka, J. Chem. Phys. 24, 915 (1956); 40, 558 (1964).

FIG. 6. Photoionization efficiency curve of $C_4H_5^+$ from 1,3-butadiene. Vertical scale is in arbitrary units and horizontal scale in electron volts.
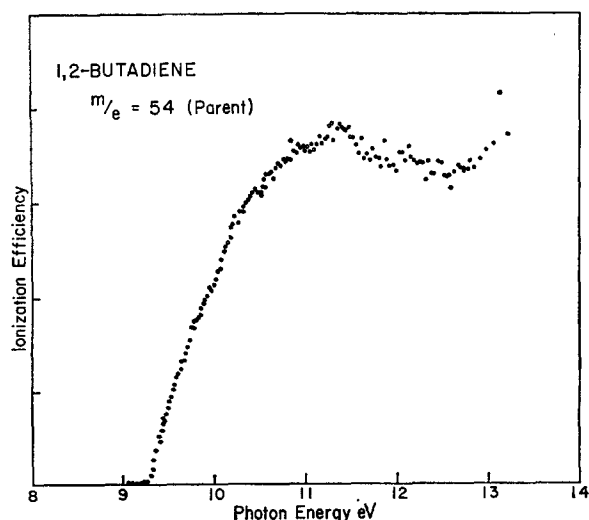

FIG. 8. Photoionization efficiency curve of 1,2-butadiene. Vertical scale is in arbitrary units and horizontal scale in electron volts.

Price and Walsh. The structure between 10.4 and 11.5 observed in the present work correlates with the positions of Rydberg series lines reported by Price and Walsh. It thus suggests that the series reported by Price and Walsh refers to an excited state of the ion.

Beyond the series limit at 11.30 eV discussed above, the photoionization efficiency drops off, and then flattens. Here, and continuing above the dissociation limit, the curve continues to exhibit a partially resolved structure characteristic of autoionization.

Figure 3 gives the ionization efficiency curve for allene. We interpret the threshold as corresponding to an adiabatic ionization potential of 9.62±0.04 eV. Above threshold the ionization efficiency curve in-

creases fairly smoothly with some contributions from autoionization. The curve breaks at about 11.5 eV. By reference to Fig. 4, it is clear that this corresponds to the threshold for fragmentation. A little below 13 eV both the parent and the fragment curve increase, strongly indicating the presence of an excited state of the ion.

Sutcliffe and Walsh[8] reported a Rydberg series in allene which converges to 10.19 eV. They interpreted the series limit as the ionization potential. This is to be compared to the present value of 9.62±0.04 eV. Clearly the Sutcliffe and Walsh series refers to an excited state of the ion. The small autoionization peaks occurring on
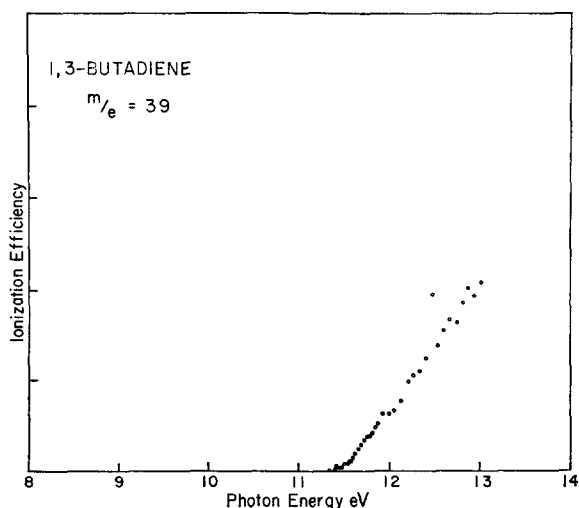

FIG. 7. Photoionization efficiency curve of $C_3H_3^+$ from 1,3-butadiene. Vertical scale is in arbitrary units and horizontal scale in electron volts.
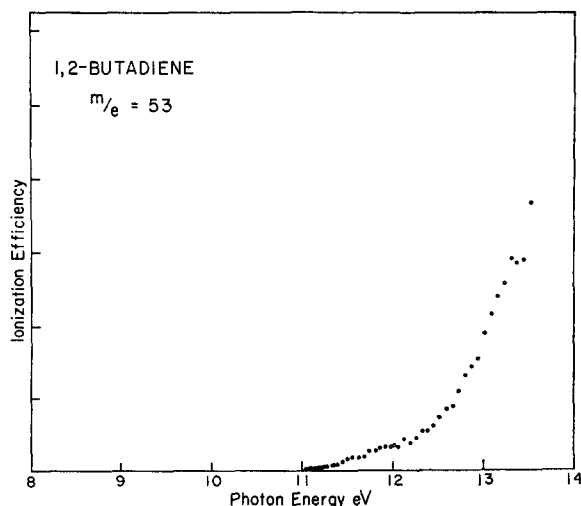

FIG. 9. Photoionization efficiency curve of $C_4H_5^+$ from 1,2-butadiene. Vertical scale is in arbitrary units and horizontal scale in electron volts.

[8] L. H. Sutcliffe and A. D. Walsh, J. Chem. Soc. 1952, 899.

the parent curve could well be the same series, but since the analysis is inconclusive, this is only suggestive.

It was pointed out by Collin and Lossing[1] that the ionization potential of allene did not agree with the idea that the diolefin ought to have a lower ionization potential than its corresponding olefinic, paraffinic, and acetylenic molecules. The more precise measurement reported here indicates that allene does indeed have a lower ionization potential than propylene (9.73 eV),[9] propane (11.08 eV),[9] and propyne reported here as 10.38 eV.

The only fragments observed in propyne and allene in the energy region studied are the $C_3H_3^+$ fragments. The $C_3H_3^+$ fragment from propyne is shown in Fig. 2, and the $C_3H_3^+$ from allene is shown in Fig. 4. The thresholds given in Table I are room-temperature thresholds. No corrections are included for temperature shift or kinetic shift since both are small and in opposite directions.

The parent curve for 1,3-butadiene is given in Fig. 5. Above the adiabatic ionization onset at 9.07 eV, a series of incompletely resolved steps and peaks occur. At about 9.80 eV, the ionization efficiency starts to decrease. At 10.2 eV, the ionization efficiency again starts to increase through a series of steps and incompletely resolved peaks. This second series of steps terminates at about 11.7 eV at which point the ionization efficiency decreases rather abruptly and continues with a line structure characteristic of autoionization. These rapid decreases cannot be attributed to competition with the fragment ions observed. Figures 6 and 7 give the $C_4H_5^+$ and $C_3H_3^+$ fragment ions from 1,3-butadienes. The $C_4H_5^+$ ion has an appearance potential

of 11.56 eV and the $C_3H_3^+$ ion has an appearance potential of 11.40 eV, hence neither onset can be correlated with the rapid decreases in the parent-ion intensity. An interpretation which can explain this structure is that the rapid decrease at 9.80 and 11.7 eV represent limits of autoionizing levels which terminate in excited states of the ion. It is to be noted that the initial structure observed in 1,3-butadiene is very similar to that observed in propyne where it is confirmed that the structure is due to autoionizing levels leading to an excited state of the ion. Using this interpretation, it appears that there are two series that go to a limit of 9.80 eV and which obey Rydberg formulas of the form

$$E = 9.80 - R/(n-0.2)^2 \qquad n = 5, 6, 7,$$
$$E = 9.80 - R/(n-0.7)^2 \qquad n = 6, 7, 8.$$

It appears that there is at least one series of lines going to a limit at 11.70 which obeys a formula of the form

$$E = 11.7 - R/(n-0.65)^2 \qquad n = 6, 7, 8, 9.$$

To refine these tentatively identified series and their limits, data will have to be taken at higher resolution.

Figure 8 shows that 1,2-butadiene has what appears to be an adiabatic ionization potential at 9.23±0.02 eV. No spectroscopic value exists with which to compare this value. Above ionization onset, the ionization efficiency curve rises through a series of partially resolved vibrational or electronic states (or both) of the ion. The interpretation of this relatively minor structure is at this time uncertain and could perhaps be clarified with higher-resolution studies. The $C_4H_5^+$ fragment and the $C_3H_3^+$ fragment from 1,2-butadiene are shown in Figs. 9 and 10, respectively. The increase in the ionization efficiency, beginning about 12.5 eV in the parent and especially in the mass 53 fragment, shows the presence of an excited state of the ion. An interesting point is the strong autoionization peaks occurring in the mass 39 fragment between 12.5 and 13.5 eV which do not appear in the parent. Clearly in this case the electron emitted in autoionization carries away relatively little energy.

DISCUSSION AND INTERPRETATION

1,3-Butadiene and 1,2-Butadiene

The heat of formation of a fragment ion is given by:
ΔH_f(fragment ion) = A.P.(fragment ion) + ΔH_f(parent molecule) − ΔH_f(neutral fragment) − kinetic shift.

Using ΔH_f(1,3-butadiene) = 1.14 eV,[10] ΔH_f(1,2-butadiene) = 1.68 eV,[10] ΔH_f(H) = 2.26[11] we calculate the
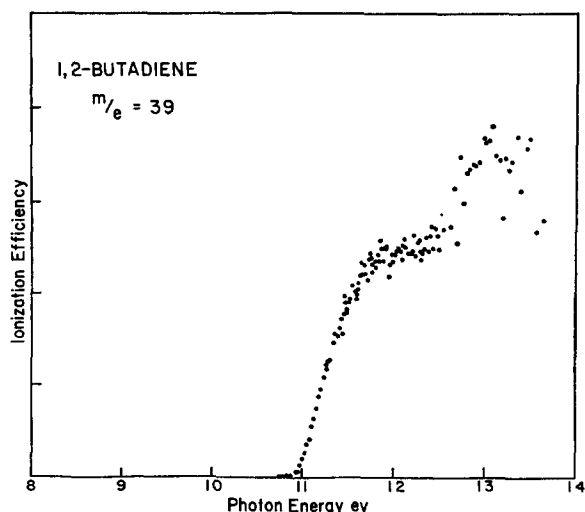

FIG. 10. Photoionization efficiency curve of $C_3H_3^+$ from 1,2-butadiene. Vertical scale is in arbitrary units and horizontal scale in electron volts.

[9] K. Watanabe, J. Chem. Phys. **26**, 542 (1957).

[10] M. M. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* (Carnegie Press, Pittsburgh, Pa., 1953).

[11] F. A. Elder, thesis, Chemistry Department, University of Chicago, 1968.

Compound	Bond	Energy
1,2-Butadiene	$C_4H_5^+$–H	1.81 eV
1,3-Butadiene	$C_4H_5^+$–H	2.39 eV
1,2-Butadiene	$C_3H_3^+$–CH_3	1.67 eV
1,3-Butadiene	$C_3H_3^+$–CH_3	2.33 eV
Allene	$C_3H_3^+$–H	1.86 eV
Propyne	$C_3H_3^+$–H	1.17 eV

heat of formation of the $C_4H_5^+$ ions to be

$$\Delta H_f(C_4H_5^+)_{1,3} = 10.44 \pm 0.04 \text{ eV} - \delta_{1,3},$$

$$\Delta H_f(C_4H_5^+)_{1,2} = 10.46 \pm 0.04 \text{ eV} - \delta_{1,2},$$

where the δ's refer to the kinetic shift appropriate to the process. Using $\Delta H_f(CH_3) = 1.39$ eV, we find the heat of formation for the $C_3H_3^+$ ions to be

$$\Delta H_f(C_3H_3^+)_{1,3} = 11.13 \pm 0.04 \text{ eV} - \delta_{1,3},$$

$$\Delta H_f(C_3H_3^+)_{1,2} = 11.15 \pm 0.04 \text{ eV} - \delta_{1,2}.$$

From the equivalence of the heat of formation of the $C_4H_5^+$ fragment ions and the $C_3H_3^+$ fragment ions from both parent systems, it is concluded that the fragment ions are the same from both systems. The $C_3H_3^+$ fragment ion from 1,2-butadiene corresponds to a direct bond-breaking reaction; however, loss of methyl in 1,3-butadiene requires a rearrangement of the parent molecule ion. This proposed rearrangement has been studied by other workers[1,2] using electron-impact techniques. It could be argued that the $C_3H_3^+$ fragment ion from 1,3-butadiene is formed during fragmentation by a CH_2 group stripping an H atom leaving the $C_3H_3^+$ ion remaining. However, if this were true, it would be expected that the methyl radical and $C_3H_3^+$ would have some degree of vibrational excitation and hence the apparent heat of formation of $C_3H_3^+$ would be different from the two molecules. The data thus support the suggestion[1,4] of hydrogen mobility. This does not say that hydrogen mobility occurs at threshold for ion formation, only that it occurs before fragmentation, i.e., the threshold for mobility is ≤ 2.34 eV.

As noted above, the heat of formation of the $C_4H_5^+$ ion from 1,3-butadiene and 1,2-butadiene are the same. These processes occur at higher energy than the threshold for formation of the $C_3H_3^+$ ions. This may indicate that simple hydrogen loss from 1,3-butadiene occurs from the same rearranged molecular-ion state postulated to explain the methyl loss.

Table III gives the derived bond energies for the molecule ions. Bond energies are taken to mean that amount of energy needed to produce the given fragment process measured from the ground electronic state of the molecule ion.

Allene and Propyne

Using ΔH_f(propyne) $= 1.92$ eV[10] and ΔH_f(allene) $= 1.99$ eV,[10] the calculated heat of formation of the $C_3H_3^+$ fragment ions from these molecules are

$$\Delta H_f(C_3H_3^+) \text{ allene} = 11.21 \pm 0.02 - \delta_a,$$

$$\Delta H_f(C_3H_3^+) \text{ propyne} = 11.21 \pm 0.02 - \delta_p.$$

The equivalence of the heat of formation of these fragment ions indicates that they are the same ion. In fact, to within the experimental error and variance of the kinetic shift, they are the same as the $C_3H_3^+$ ions observed in the butadienes. The derived bond energies for H loss are given in Table III for the allene and propyne systems.

CONCLUSIONS

Definitive statements about rearrangement cannot be made by photoionization mass spectrometry alone, unless it is possible to show that a proposed rearrangement is energetically impossible.[11] The usefulness of photoionization mass spectrometry is in the precise determination of heat of formation and electronic energy levels which may be used to formulate the energetics of proposed mechanisms of rearrangement.

The measurements here indicate that the proposed rearrangement in 1,3-butadiene by hydrogen migration during or before fragmentation is certainly energetically possible. The rearrangement can energetically first take place at 9.77 eV, where the total energy of the 1,3-butadiene molecule–ion is degenerate with the total energy of the ground state of 1,2-butadiene. The excited state identified at 9.80 eV comes in at this energy and may contribute to the rearrangement mechanism.

ACKNOWLEDGMENT